HAIR CARE PRODUCT PROVIDING SHINE

TECHNICAL FIELD

This invention relates to hair care products containing a composition that through the use of certain silicones and ethanol provides shine to the hair, and additionally provide a clean hair feel and refreshing hair and scalp feel. This invention further relates to such hair care products described above that provide such benefits and contain ethanol without causing the scalp to become dried-out.

BACKGROUND OF THE INVENTION

The shampooing of hair conventionally is performed utilising any of numerous detersive surfactant-containing compositions known in the art. However the combination of frequent shampooing, environmental factors, and the natural condition of one's hair can result in the hair not having a healthy, lusturous appearance. One of the most effective ways of addressing this problem is through the use of hair conditioning compositions that improve the shine of the hair. A highly effective technology for this purpose is the use of a combination of a high refractive index polysiloxane fluid, such as phenylated polysiloxane, with a spreading agent, such as a polysiloxane resin, as disclosed in WO 94/08557 (Brock et al., Procter & Gamble, published April 28, 1994).

It is also highly desirable to provide hair treatment compositions, especially leave-on compositions, that impart a clean feeling, or sense of refreshment, to the scalp. This is most especially important for leave-on hair care product containing the above combination of phenylated silicone and spreading agent since they can impart to the hair a coated feeling that is not especially desirable on the part of the consumer. This problem is exacerbated by leave-on products. Although leave-on products are highly desirable from the standpoint of providing excellent shine to the hair versus rinse-off products, they

can result in excess phenylated silicone/spreading agent being left on the hair, and this can have detrimental effects upon clean hair feel. . Sensates such as menthol and camphor can be used in leave-on products to increase the sense of refreshment, however these do not totally overcome the issue of overall refreshment, which must include a solution the hair feeling coated by the phenylated silicone/spreading agent combination. It has been found that under certain conditions one of the most effective and desirable ingredients for this purpose is ethanol. Ethanol, however must be used at relatively high levels in order to achieve maximum levels of refreshment and clean hair feel. Unfortunately when used at these levels, ethanol can cause the scalp to become dried out, leading to the skin feeling itchy or to suffer from flaking.

It is an object of this invention to provide hair care compositions, especially leave-on compositions, that can provide excellent shine while at the same time providing a clean refreshing feel to the hair and scalp while also minimizing or eliminating drying-out out the scalp.

The above object can be achieved through the use of a combination of a shine agent comprising a high refractive index silicone fluid and a spreading agent, in conjunction with particular levels of ethanol, and further when delivered to the hair in certain product forms. The present invention shall be described in further detail below.

All percentages herein are by weight of the composition unless otherwise indicated. All ratios are weight ratios unless otherwise indicated. Unless otherwise indicated, all percentages, ratios, and levels of ingredients referred to herein are based on the actual amount of the ingredient, and do not include solvents, fillers, or other materials with which the ingredient may be combined as commercially available products.

The invention hereof can comprise, consist of, or consists essentially of the essential elements described herein as well as any of the preferred or other optional ingredients described herein.

SUMMARY OF THE INVENTION

It has now been found that hair care products containing a composition providing enhanced shine to the hair in combination with clean hair feel and refreshment without inducing excess drying-out of the scalp can be provided through the combination of: (a) a hair shine agent consisting essentially of: (i) a high refractive index non-volatile polysiloxane fluid and (ii) a non-volatile spreading agent for the high refractive index

polysiloxane fluid which is intermixed with the high refractive index polysiloxane fluid; (b) ethanol; and (c) water; wherein the ethanol level is from about 10% to about 50%, by weight, of the composition.

In another aspect of the present invention, the composition hereof further comprises a scalp conditioning agent.

Suitable spreading agents include, but are not necessarily limited to, silicone resins (especially MQ silicone resins), surfactants such as polyether siloxane copolymers and non-silicone-containing organic surfactants.

The present invention also relates to a method for providing shine to the hair, by use. The compositions hereof are preferably leave-on compositions, and therefore the preferred method of use provides for allowing the composition to dry on the hair without first being rinsed off.

The compositions and methods of the present invention are advantageous for utilization in connection with a wide variety of the hair care products, especially leave-on compositions, such as hair lotions, tonics, gels, creams, and certain sprays. The spray products, which can include aerosol and nonaerosol sprays, e.g., hair sprays, mousses, etc., are characterized by having at least 40%, by volume, of the spray droplets having a particle size of at least 100 microns. The percentage by volume as used herein refers to the percentage of fluid sprayed having particles size within the referenced level based on the total fluid volume sprayed.

Another benefit of the present invention is that the compositions hereof can provide a clean, refreshing sensation to the scalp in combination with clean hair feel, refreshing hair and scalp sensation, and hair shine. The compositions hereof can also be characterized as providing low levels of tackiness and greasiness while providing excellent shine and low scalp dryness. The present compositions can also provide conditioning to the hair through the use of the shine agent as well as through the use of additional ingredients as well be described below.

The present invention including various nonlimiting optional and preferred embodiments thereof, is described in more detail below.

DETAILED DESCRIPTION OF THE INVENTION

The essential components and aspects of the invention, as well as various optional and preferred ingredients and embodiments of the invention, are described below.

Hair Care Product

The invention hereof relates to a hair care product comprising a hair care composition which is suitable for application to the hair. The hair care products hereof can also comprise a package for containing the composition.

A wide variety of suitable packages are known in the art. They will generally be characterized by dispensing orifices through which the product can be poured, shaken, pumped, squeezed, or sprayed.

The products hereof are preferably leave-on products. By leave-on product is meant that the composition is applied to the hair and allowed to remain on the hair to dry without first being rinsed off. The leave-on products can be of any type suitable and intended to be applied to the hair and used in a leave-on manner. Without limitation, these include tonics, gels, creams, pastes, and sprays (aerosols, nonaerosols) including hair sprays which condition and/or style the hair.

The leave-on products hereof will be free of cleansing-effective levels of cleansing surfactants, such as anionic and amphoteric surfactants, which are generally present in compositions such as shampoos. In general leave-on compositions will contain no more than about 5% of such surfactants, preferably no more than about 3 %, more preferably no more than about 1%, most preferably no more than about 0.5 % and can be as low as zero per cent.

The leave-on products hereof can also include with their packaging instructions in the manner of use consistent with leave-on products, such as described in more detail below in the section relating to method of use.

By "spray" what is meant herein is a product that upon use dispenses the composition in the form of droplets dispersed in the ambient air (liquid-in-gas dispersion). The spray products hereof will comprise compositions which are characterized by having at least about 40%, by volume, of the sprayed droplets having a particle size of at least 100 microns. Preferably at least 50%, more preferably at least 70%, most preferably at least 80%, of the spray droplets will have a particle size of at least 100 microns. Spray droplet particle size is determined by laser diffraction (such as with a Malvern Instruments 2600C particle size analyzer or equivalent) using the International Organization for Standardization (ISO) Standard Method ISO/WD 13320. Particle size refers to diameter. Without intending to be limited by theory, it is believed that smaller

spray particles do not sufficiently penetrate throughout the entire depth of the hair, and consequently suffer from insufficient distribution in order for the composition to provide the desired levels of performance. It is to be understood that the spray products do not include mousses, which although they can be dispensed via aerosol or nonaerosol packages, they do not actually provide a dispersion of droplets in ambient air in the same manner as a conventional spray.

The compositions can be solutions, liquid-in-liquid dispersions, emulsions, micro-emulsions, liquid crystalline, or any other form except as indicated below, suitable for application to the hair and scalp.

Without limitation as to theory, it is believed that a mousse instead dispenses product in a form wherein gas (e..g., propellant and/or air) is dispersed throughout the composition, i.e., mousses are dispensed in the form of gas-in-liquid dispersions. Furthermore, gas-in-liquid dispersions such as mousses generally do not provide the benefits or fulfil the objects of the present invention in that they are inferior for providing a clean hair feel, and therefore mousses and other hair care products that upon use provide gas-in-liquid dispersions are excluded from the scope of this invention.

Hair Shine Agent

The compositions of the present invention comprises a hair shine agent which consists essentially of a high refractive index, nonvolatile polysiloxane fluid and a spreading agent for the high refractive index polysiloxane fluid. These two ingredients will be intermixed in the same phase of the composition The hair shine agent will generally be present at a level of from about 0.05% to about 10%, by weight, of the composition, preferably from about 0.1% to about 5%, more preferably from about 0.2 % to about 2%. By "consisting essentially of" what is meant is that the hair shine agent must contain the indicated essential ingredients, but that it can also contain other ingredients which do not prevent the composition hereof from functioning in its intended manner. The total level of the two essential ingredients will preferably be within the same ranges given above for the hair shine agent.

High Refractive Index Non-volatile Polysiloxane Fluid

The compositions of the present invention contain as an essential ingredient a non-volatile polysiloxane fluid ('Silicone fluid') having a refractive index of at least about 1.46, preferably at least about 1.48, more preferably at least about 1.52, most preferably at

lease about 1.55. Although not intended to necessarily limit the invention, the refractive index of the polysiloxane fluid will generally be less than about 1.70, typically less than about 1.60.

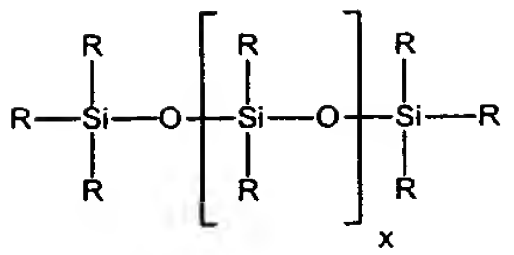
As is well known in the art, refractive index refers to the change in direction (i.e. apparent bending) of a light ray passing from one medium to another. Refractive index shall herein refer to the light ray passing from air to the polysiloxane fluid or polysiloxane fluid/spreading agent mixture. Refractive index of the silicone fluid can be determined using standard equipment commonly available and known in the art, such as a Abbe refractometer. Techniques for measuring refractive index are described in the Handbook of Chemical Microscopy, Volume 1 - Chemical Methods and Inorganic Qualitative Analysis, Chemot and Mason, ed, John Wiley & Sons,Inc., New York, 1958, pp 311-334.

The term 'non-volatile' as used herein means the material referred to exhibits very low or no significant vapor pressure at ambient conditions, as well-known and understood in the art. Non-volatile materials will generally exhibit no more than 0.2mm Hg at 25°C and one atmosphere. Non-volatile materials will also generally have a boiling point at one atmosphere of at least 275°C, preferably at least 300°C.

The polysiloxane fluid for use herein will generally have viscosity of at least about 10 centistokes at 25°C, preferably from about 20 to about 2,000,000 centistokes, more preferably from about 30 to about 500,000 centistokes. Other viscosity non-volatile silicone fluids can also be used in the present invention as long as the other requirements described herein are met. In general, of conditioning as well as hair shine is desired from the silicone fluid, higher viscosity materials such as those above about 50,000, preferably above about 100,000, are preferably used. The viscosity can be measured by means of a glass capillary viscometer as set forth in Dow Corning Corporate Test Method CTM0004, July 20, 1970. Polysiloxane 'fluid' as used herein includes fluids as well as gums. Polysiloxane "gums" refer to polysiloxanes having viscosity of about 1,000,000 centistoke or greater.

The polysiloxane fluid suitable for purposes hereof includes those represented by general Formula (I):

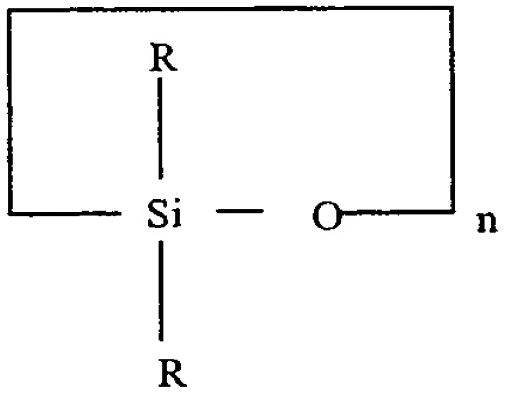
(I)



wherein each R, independently is substituted or unsubstituted aliphatic (e.g. alkyl or alkenyl), aryl, aryloxy, alkaryl, alkoxy, alkamino (e.g. alkyl or alkenyl amino groups), hydroxy, or hydrogen, or combinations thereof; and x is an integer of at least about 1, typically from about 1 to about 1,000. The R substituents can also include combinations of ether groups, hydroxy groups, and amine groups, as well as other functional groups, such as halogens and halogen-substituted functionalities, e.g. halogen-substituted aliphatic and aryl groups.

The polysiloxane fluid can be cyclic or linear. Linear polysiloxanes are exemplified above by Formula I. Branched chain can also be used. Cyclic polysiloxanes include those represented by Formula (II):

(II)



wherein R is as defined above, $_n$ is from about 3 to about 7, preferably from three to five.

The substituents on the siloxane chain (R) may have any structure as long as the resulting polysiloxanes remain fluid at room temperature, are hydrophobic, are neither irritating, toxic nor otherwise harmful when applied to the hair, are compatible with the other components of the composition are chemically stable under normal use and storage conditions, are capable of being deposited on the hair, and the resulting polysiloxane fluid has a refractive index as set forth above.

Preferred alkyl and alkenyl substitutes are C_1-C_5 alkyls and alkenyls, more preferably from C_1-C_4, most preferably from C_1-C_2. The aliphatic portions of other alkyl-, alkenyl-, or alkynyl- containing groups (such as alkoxy, alkaryl and alkamino) can be straight or branched chains and preferably have from one to five carbon atoms, more preferably from one to four carbon atoms, even more preferably from one to three carbon atoms, most preferably from one to two carbon atoms. As discussed above, the R Substituents hereof can also, contain amino functionalities, e.g., alkamino groups, which can be primary, secondary or tertiary amines or quaternary ammonium. These include mono-, di-, and tri- alkylamino and alkoxyamino groups wherein the aliphatic portion chain length is preferably as described above. The R substituents can also be substituted with other groups, such as halogens (e.g. chloride, fluoride, and bromide) halogenated aliphatic or aryl groups and hydroxy (e.g. hydroxy substituted aliphatic groups). Suitable halogenated R groups could include for example, tri-halogenated (preferably fluoro) alkyl groups such as $-R^1-C(F)_3$, wherein R^1 is C_1-C_3 alkyl. Examples of such polysiloxanes include polymethyl -3,3,3, trifluoropropylsiloxane.

The high refractive index polysiloxane fluids hereof contain a sufficient amount of aryl-containing R substituents to increase the refractive index to the desired level, which is described above.

Aryl-containing substituents contain alicyclic and hererocyclic five and six membered aryl rings, and substituents containing fused five or six membered rings. The aryl rings themselves can be substituted or unsubstituted. Substituents include aliphatic substituents, and can also include alkoxy substituents, acyl substituents, ketones, halogens (e.g. CL and BR), amines, etc. Exemplary aryl-containing groups include substituted and unsubstituted arenes, such as phenyl, and phenyl derivatives such as phenyls with C_1-C_5 alkyl or alkenyl substituents, e.g., allylphenyl, methyl phenyl and ethyl phenyl, vinyl phenyls such as styrenyl, and phenyl alkynes (e.g. phenyl C_2-C_4 alkynes). Heterocyclic aryl groups include substituents derived from furan, imadazole, pyrrole, pyridine, etc. Fused aryl ring substituents include, for example napthalene, coumarin and purine.

In general, the polysiloxane fluids hereof will have a degree of aryl-containing substituents of at least about 15%, preferably at least about 20%, more preferably at least about 25%, even more preferably at least about 35%, most preferably at least about 50%. Typically, although it is not intended to necessarily limit the invention, the degree of aryl

substitution will be less than about 90%, more generally less than about 85%, preferably from about 55% to about 80%.

The polysiloxane fluids hereof are also generally characterised by relatively high surface tensions as a result of their aryl substitution. In general, the polysiloxane fluids hereof will have a Surface Tension of at least about 24 dynes/cm^2, typically at least about 27 dynes/cm^2. Surface Tension, for purposes hereof, is measured by a de Nouy ring tensionmeter according to Dow Corning Corporate Test Method CTM 0461, November 23, 1971. Changes in Surface Tension can be measured according to the above test method or according to ASTM Method D 1331. The preferred polysiloxane fluids hereof will have a combination of phenyl or phenyl derivative substituents (preferably phenyl), with alkyl substituents, preferably C_1-C_4 alkyl (most preferably methyl) hydroxy, alkanamino (especially -R^1NHR^2NH2 where each R^1 independently is a C_1-C_3 alkyl, alkenyl, and/or alkoxy.

High refractive index polysiloxane are available from Dow Corning Corporation (Midland, Michigan, USA) Huls America (Piscataway, New Jersey, USA), General Electric Silicones (Waterford, New York, USA).

Spreading Agent

The compositions of the present invention will also comprise a nonvolatile spreading agent for the polysiloxane fluid. The spreading agent hereof must be compatible with the polysiloxane fluid.

The term 'non-volatile' is defined previously herein. By 'compatible' what is meant is that the spreading agent is soluble in, dispersible in, or miscible with the polysiloxane fluid, such that these two components can remain intermixed in the same phase of the composition. The spreading agent and the polysiloxane fluid are intermixed in the composition to form a mixture whereby the spreading agent reduces the Surface Tension of the polysiloxane fluid. Surface Tension reductions can be determined according to the procedure described previously herein. The spreading agent and polysiloxane fluid phase hereof can be a continuous or discontinuous phase in the present compositions.

The composition hereof should preferably contain a sufficient amount of the spreading agent to reduce the Surface Tension of the polysiloxane fluid by at least about 5%, preferably at least about 10%, more preferably at least about 15%, even more

preferably at least about 20%, most preferably at least about 25%. Reductions in Surface Tension of the polysiloxane fluid/spreading agent mixture can provide improved shine enhancement of the hair.In the most preferred compositions hereof Surface Tension will e reduced by from about 20% to about 35%, more generally from about 25% to about 30%.

Also preferably the spreading agent should reduce the Surface Tension by at least about 2 dynes/cm^2, more preferably at least about 3 dynes/cm^2, even more preferably at least about 4 dynes/cm^2, most preferably at least about 5 dynes/cm^2.

The Surface Tension of the mixture of the polysiloxane fluid and the spreading agent, at the proportions present in the final product, is preferably 30 dynes/cm^2 or less, more preferably about 28 dynes/cm^2 or less most preferably about 25 dynes/cm^2 or less. Typically the Surface Tension will be in the range of from about 15 to about 30, more typically from about 18 to about 28, and most generally from about 20 to about 25 dynes/cm^2.

Gloss is a physical attribute that contributes to the shine appearance of an object. Gloss can be measured in terms of specular reflectance. Specular reflectance refers to the fraction, or percentage, of incident light reflected from a surface in the mirror direction (i.e. the light reflected in the direction that is 108° from the light flowing from the light source toward the reflective surface) within a specified angular tolerance. Specular reflectance is a useful means for measuring shininess of hair. Further background is specular reflectance and its use in evaluating shininess of hair can be found in R F Stamm, M L Garcia and J J Fuchs, 'The Optical Properties of Human Hair-I. Fundamental Consideration and Goniophotometer Curves, and II. The Lustre of Human Hair Fibres', J Soc. Cosmet. Chem. 28, 571-599 and 601-609 (September 1977) all incorporated herein by reference.

Specular reflectance measured from a coating of the compositions hereof on a collagen-coated black ceramic plate correlates with shininess on hair and is less suspect to experimental variations due to inconsistency between hair samples and deposition of the hair shine agent. Specular reflectance on such collagen-coated black ceramic plates as measured in the present invention is determined accordingly that the procedure below in the Experimental and is referred to herein as Glossmeter Spectular Reflectance.

The present invention can alternately be described in terms of compositions containing a mixture of the spreading agent and the polysiloxane fluid wherein the

composition contains a sufficient amount of the spreading agent to increase the Glossmeter Specular Reflectance for the mixture, relative to the polysiloxane fluid by at least about 'delta 1.0% (hereinafter "Δ 1.0%" wherein delta refers to a change in percentage specular reflectance based upon 100% of the original light intensity). Preferably, the increase in Glossmeter Specular Reflectance is at least Δ 2.0%, more preferably at least about Δ 5.0%, even more preferably at least about Δ 7.5%, most preferably at least about Δ 10.0%.

Glossmeter Specular Reflectance is measured according to the procedure described below in the Experimental. In general, a 1.0% solution of the polysiloxane fluid in the same solvent, if any, used in the same phase as the polysiloxane fluid in the composition is used. If the polysiloxane fluid is not diluted with a separate solvent in the composition, cyclimethicone should be used to prepare the 1.0% solution. If the necessary cyclomethocone ethanol solutions can be used to form the 1.0% of polysiloxane for purposes of the test. For the control no spreading agent is incorporated. Otherwise, spreading agent is incorporated into the solution at the same weight ratio of polysiloxane fluid to spreading agent as present in the composition. The test solution is deposited on a collagen-coated, black ceramic tile and allowed to dry. Specular reflectance is measured with a glossmeter, a spectrophotometer suitable for measuring specula reflectance form flat surfaces. Suitable glossmeters are commercially available and known in the art, e.g. the 'micro-gloss' glossmeter available from BYK-Gardner, Ind, Silver Spring , MD, USA.

The weight ratio of polysiloxane fluid to the spreading agent will, in general, be between about 1000:1 and about 1:10, preferably between about 100:1 and about 1:1, more preferably between about 50:1 and about 2:1, most preferably from about 25:1 to about 2:1. For hair rinse compositions it is particularly preferred for the ratio to be between about 10:1 and about 2:1. When fluorinated surfactants are used, particularly high polysiloxane; spreading agent ratios may be effective due to the efficiency of these surfactant. Thus, it is contemplated that ratios significantly above 100:1 may be used.

Preferred spreading agents for use herein include silicone resins, and surfactants, which include booth polyether siloxane copolymers and non-silicone-containing organic surfactants. Especially preferred spreading agents are the silicone resins.

Silicone Resin

Silicone resins are highly crosslinked polymeric siloxane systems. The crosslinking is introduced through the incorporation of trifunctional and tetra functional silanes with monofunctional or difunctional monomer units, or both during manufacture of the silicone resin. As is well understood in the art, the degree of crosslinking that is required in order to result in a silicone resin will vary according to the specific silane units incorporated into the silicone resin. In general, silicone materials which have a sufficient level of trifunctional and tetrafunctional siloxane monomer units (and hence, a sufficient level of crosslinking) such that they dry down to a rigid, or hard film are considered to be silicone resins. The ratio of oxygen atoms to silicon atoms is indicative of the level of crosslinking in a particular silicone material. Silicone resins will generally have at least about 1:1 oxygen atom per silicone atom. Preferably, the ratio of oxygen:silicon atoms is at least about 1.2:1.0. Typical silanes used in the manufacture of silicone resins are the monomethyl-, dimethyl-, monophenyl-, diphenyl-, methylphenyl-, monovinyl-, and methylvinyl-chlorosilanes, and tetrachlorosilane. Preferred resins are the methyl substituted silicone resins, such as those offered by General Electric as GE SS4230 and SS4267. Commercially available silicone resins will generally be supplied in an unhardened form in a low viscosity volatile or, preferably non-volatile silicone fluid. The silicone resins for use herein will be present in the compositions hereof in non-hardened form rather than as a hardened resin, as will be readily apparent to these skilled in the art.

Background material on silicones including sections discussing silicone fluids, gums and resins, as well as manufacture of silicones, can be found in Encyclopaedia of Polymer Science and Engineering, Volume 15, Second Edition, pp 204-308, John Wiley & Sons Inc 1989 and Chemistry and Technology of Silicones, Walter Noll, Academic Press Inc, (Harcourt Bruce Javanovich, Publishers, New York), 1968, pp 282-287 and 409-426, both incorporated herein by reference.

Silicone materials and silicone resins in particular, can be identified according to a shorthand nomenclature system well known to those skilled in the art as 'MDTQ' nomenclature. Under this system, the silicone is described according to presence of various siloxane monomer units which make up the silicone. Briefly, the symbol M denotes the monofunctional unit $(CH_3)_3SiO_{.5}$, D denotes the difunctional unit $(CH_3)_2SiO$; T denotes the trifunctional unit $(CH_3)Si_{1.5}$; and Q denotes the quadri- or tetra-functional

unit SiO_2. Primes of the unit symbols, e.g. M', D', T', and Q' denotes substituents other than methyl, and must be specifically defined for each occurrence. Typical alternate substituents include groups such as vinyl, phenyls, amines, hydroxyls, etc. The molar ratios of the various units, either in terms of subscripts to the symbols indicating the total number of each type of unit in the silicone (or an average thereof) or as specifically indicated ratios in combination with molecular weight complete the description of the silicone material under the MDTQ system. Higher relative molar amounts of T, Q, T' and/or Q' to D, D', M and/or or M' in a silicone resin is indicative of higher levels of crosslinking. As discussed before, however, the overall level of crosslinking can also be indicated by the oxygen to silicone ratio.

The silicone resins for use herein which are preferred are MQ, MT, MTQ, and MDTQ resins. Thus, the preferred silicone substituent is methyl. Especially preferred are MQ resins particularly those wherein the M:Q molar ratio is from about 0.5:1.0 to about 1.5:1.0 and the average molecular weight of the resin is from about 500 to about 10,000, generally from about 1,000 to about 10,000.

Depending upon the particular choice of spreading agent (particularly the silicone resins) and polysiloxane fluid, it may be necessary or desirable to incorporate an additional solvent to ensure that the resin and polysiloxane fluid are compatible with one another. Thus, if the silicone resin isn't compatible with polysiloxane fluid at the desired polysiloxane fluid : silicone resin weight ratio, it will be useful to incorporate into the polysiloxane/spreading agent phase a solvent to facilitate enhanced solubility or dispersibiltiy of these components. If the solvent has a refractive index below about 1.46 or is otherwise below the refractive index of the polysiloxane fluid, it may be desirable to use a solvent which is volatile (materials that exhibit greater than 0.2mmHg at 25°C and one atmosphere, generally with a boiling point of less that 275° C), so that it does not remain on the hair and potentially impair the shine performance obtained according to the present invention. Suitable solvents include: cyclomethicone, other cyclic siloxanes such as those described herein as carrier fluids, linear polysiloxane polymers such as dimethicone, and other low viscosity analogues of the polysiloxane materials described in Formulas I and II, preferably having viscosity at 25° C of about 10 centisokes or less, such materials generally having lower (or zero) degree of aryl-containing substituents than the highly arylated, high refractive index polysiloxane of the present invention; volatile liquid

hydrocarbons, such as straight or branched chain hydrocarbons having from about 4 to about 16 carbon atoms (e.g., hexane, isobutane, decane, dodecane, tetradecane, tridecane); lower alcohols (e.g. C_2 -C_4 alcohols such as ethanol and isopropanol); hydrocarbon esters, preferably with a total of about 10 carbon atoms or less (e.g. ethyl acetate); halogenated hydrocarbons (e.g. freon); volatile ketones (e.g. acetone); and mixtures thereof. Especially preferred is cyclomethicone. The present invention does not, however, exclude the use of nonvolatile solvents for the resin/phenylated polysiloxane solvent.

When used, solvents as described above will be used typically at a weight ratio of (solvent) to (highly arylated nonvolatile polysiloxane plus spreading agent) of up to about 100:1, more typically up to about 50:1, for rinse-off hair care products, preferably from about 2:1 to about 10:1 for hair rinse products. For leave-on products, high levels of volatile solvents may be used as carrier ingredients, as described later.

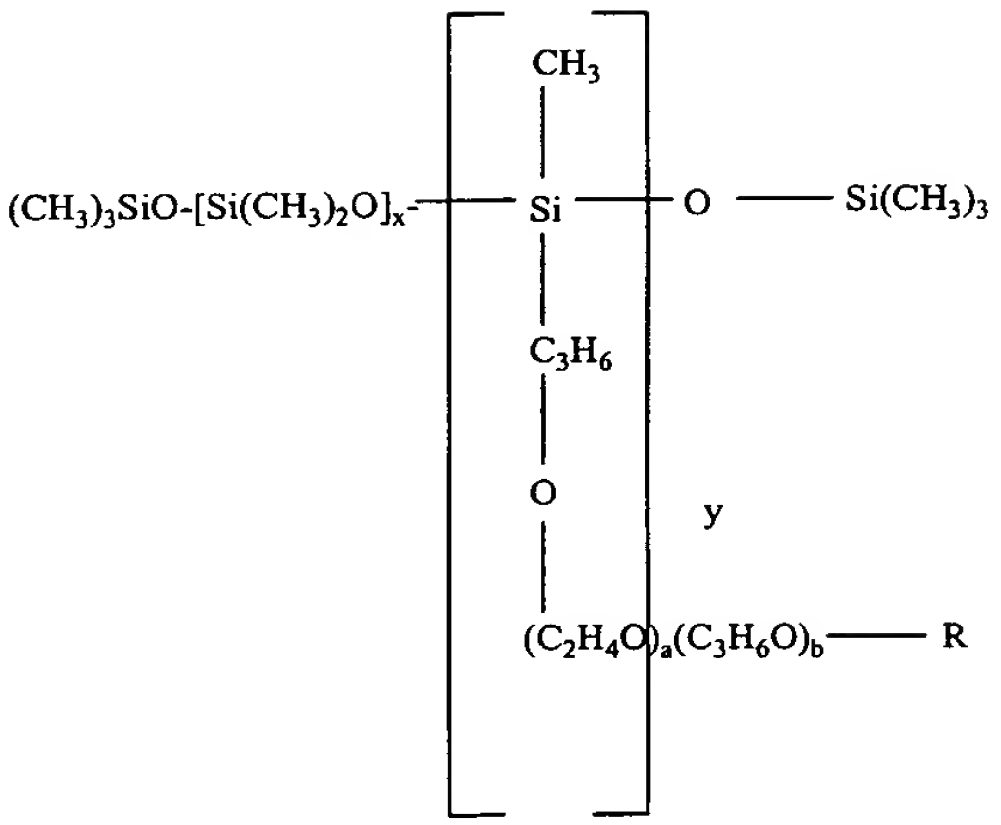
Surfactants

Surfactants that are compatible with the polysiloxane fluid hereof and which is suitable for application to the hair can also be used as a spreading agent. The surfactants can be anionic, cationic, nonionic, amphoteric, or a zwitterionic.

Polyether Siloxane Copolymer

Polyether siloxane copolymers, or silicone "copolyols" as they are sometimes referred to, are silicone-containing surfactants that can be utilized as spreading agents for the polysiloxane fluid. Silicone copolyols are surfactants charecterized by a hydrophobic polysiloxane chain and a hydrophilic alkoxy portion.

Silicone copolyols which may be used include polyalkylene oxide modified polydimethylsiloxanes of the following formulae:



and

$$R' - Si - - [- O Si (CH_3) 2]_x - (OC_2H_4)_a - (OC_3H_6)_b - _3 OR''$$

wherein R is hydrogen, an alkyl group having from 1 to about 12 carbon atoms, an alkoxy group having from 1 to about 6 carbon atoms or a hydroxyl group; R' and R" are alkyl groups having from 1 to about 12 carbon atoms; x is and integer of from 1 to 100, preferably from 20 to 30; y is an integer of 1 to 20, preferably from 2 to 10; and a and b are integers of from 0 to 50, preferably from 20 to 30.

Silicone copolyols among those useful herein are also disclosed in the following patent documents, all incorporated by reference herein: U.S. Patent 4,122,029, Geen, et al., issued October 24, 1978; U.S. Patent 4,265,878, Keil, issued May 5, 1981; and U.S, Patent 4,421,769, Dixon, et al., issued December 20, 1983. Such silicone copolyol materials are also disclosed, in hair compositions, in British Patent Application 2,066,659, Abe, published July 15, 1981 (incorporated by reference herein) and Canadian Patent 727,588, Kuehns, issued February 8, 1966 (incorporated by reference herein). Commercially available silicone copolyols which can be used herein, include Silwet Surface Active Copolymers (manufactured by the Union Carbide Corporation); and Dow Corning Silicone Surfactants (manufactured by the Dow Corning Corporation).

A variety of suitable non-silicone-containing organic surfactants that can be used are described below.

Anionic Surfactants

Anionic surfactants useful herein include alkyl and alkyl ether sulfates. These materials typically have the respective formulae $ROSO_3M$ and $RO(C_2H_4O)_xSO_3M$, wherein R is alkyl or alkenyl of from about 10 to about 20 carbon atoms, x is 1 to 10, and M is a water-soluble cation such as ammonium, sodium, potassium and triethanolamine.

Another suitable class of anionic surfactants are the water-soluble salts of the organic, sulfuric acid reaction products of the general formula:

$$R_1—SO_3—M$$

wherein R_1 is chosen from the group consisting of a straight or branched chain, saturated aliphatic hydrocarbon radical having from about 8 to about 24, preferably about 12 to about 18, carbon atoms; and M is a cation. Important examples are the salts of an organic sulfuric acid reaction product of a hydrocarbon of the methane series, including iso-, neo-, and n-paraffins, having about 8 to about 24 carbon atoms, preferably about 12 to about 18 carbon atoms and a sulfonating agent, e.g., SO_3,H_2SO_4, oleum, obtained according to known sulfonation methods, including bleaching and hydrolysis. Preferred are alkali metal and ammonium sulfonated C_{12-18} n-paraffins.

Additional examples of anionic surfactants which come within the terms of the present invention are the reaction products of fatty acids esterified with isethionic acid and neutralized with sodium hydroxide where, for example, the fatty acids are derived from coconut oil; sodium or potassium salts of fatty acid amides of methyl tauride in which the fatty acids for example, are derived from coconut oil. Other anionic surfactants of this variety are set forth in U.S. Patents, 2,486,921; 2,486,922; and 2,396,278.

Still other anionic surfactants include the class designated as succinamates. This class includes such surface active agents as disodium N-octadecylsulfosuccinamate; tetrasodium N-(1,2-dicarboxyethyl)-N-octadecylsulfosuccinamate; diamyl ester of sodium sulfosuccinic acid; dihexyl ester of sodium sulfosuccinic acid; dioctyl esters of sodium sulfosuccinic acid.

Other suitable anionic surfactants utilizable herein are olefin sulfonates having about 12 to about 24 carbon atoms. The term "olefin sulfonate" is used herein to mean compounds which can be produced by the sulfonation of a-olefins by means of

uncomplexed sulfur triocide, followed by neutralization of the acid reaction mixture in conditions such that any sultones which have been formed in the reaction are hydrolyzed to give the corresponding hydroxyl-alkanesulfonates. The a-olefins from which the olefin sulfonates are derived are mono-olefins having about 12 to about 24 carbon atoms, preferably about 14 to about 16 carbon atoms. Another class of anionic organic surfactants are the b-alkyloxy alkane sulfonates.

Nonionic Surfactants

Nonionic surfactants can be broadly defined as compounds produced by the condensation of alkylene oxide groups (hydrophilic in nature) with a hydrophobic compound, which may be aliphatic or alkyl aromatic in nature. Nonlimiting examples of classes of nonionic surfactants are:

1. The polythylene oxide condensates of alkyl phenols, e.g., the condensation products of alkyl phenols having a alkyl group containing from about 6 to about 20 carbon atoms in either a straight chain or branched chain configuration, with ethylene oxide, the said ethylene oxide being present in amounts equal to from about 10 to about 60 moles of ethylene oxide per mole of alkyl phenol.

2. Those derived from the condensation of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylene diamine products.

3. The condensation product of aliphatic alcohols having from about 8 to about 18 carbon atoms, in either straight chain or branched chain configuration, with ethylene oxide e.g., a coconut alcohol ethylene oxide condensate having from about 10 to about 30 moles of ethylene oxide per mole of coconut alcohol, the coconut alcohol fraction having from about 10 to about 14 carbon atoms.

4. Long chain tertiary amine oxides such as those corresponding to the following general formula:

$$R_1R_2R_3N\text{---------}\rightarrow 0$$

wherein R_1 contains an alkyl, alkenyl or monohydroxy alkyl radical of from about 8 to about 18 carbon atoms, from 0 to about 10 ethylene oxide moieties, and from 0 to about 1 glyceryl moiety, and R_2 and R_3 contain from about 1 to about 3 carbon atoms and from 0 to about 1 hydroxy group, e.g., methyl, ethyl, propyl, hydroxyethyl, or hydroxypropyl radicals (the arrow in the formula represents a semipolar bond).

5. Long chain tertiary phosphine oxides corresponding to the following general formula:

$$RR'R''P\text{--------}\rightarrow O$$

wherein R contains an alkyl, alkenyl or monohydroxyalkyl radical ranging from about 8 to about 18 carbon atoms in chain length, from 0 to about 10 ethylene oxide moieties and from 0 to about 1 glyceryl moiety and R^1 and R^2 are each alkyl or monohydroxyalkyl groups containing from about 1 to about 3 carbon atoms. The arrow in the formula represents a semipolar bond.

6. Long chain dialkyl sulfoxides containing one short chain alkyl or hydroxyl alkyl radical of from about 1 to about 3 carbon atoms (usually methyl) and one long hydrophobic chain which include alkyl, alkenyl, hydroxy alkyl, or keto alkyl radicals containing from about 8 to about 20 carbon atoms, from 0 to about 10 ethylene oxide moieties and from 0 to about 1 glyceryl moiety.

7. Polysorbates, e.g., sucrose esters of fatty acids. Such materials are described in U.S. Patent 3,480,616, e.g., sucrose cocoate (a mixture of sucrose esters of a coconut acid, consisting primarily of monoesters, and sold under the tradenames GRILLOTEN LSE 87K from RITA, and CRODESTA SL-40 from Croda).

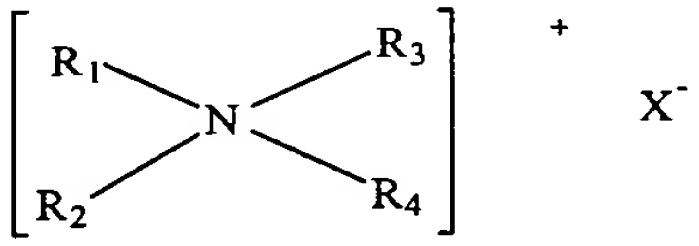
8. Alkyl polysaccharide nonionic surfactants are disclosed in U.S. Patent 4,565,647. Llenado, issued January 21, 1986, having a hydrophobic group containing from about 6 to about 30 carbon atoms, preferably from about 10 to about 16 carbon atoms and a polysaccharide, e.g., a polyglycoside, hydrophilic group. Any reducing saccharide containing 5 or 6 carbon atoms can be used, e.g., glucose, galactose and galactosyl moieties can be substituted for the glucosyl moieties. Optionally there can be a polyalkyleneoxide chain joining the hydrophobic moiety and the polysaccharide moiety. The alkyl group preferably contains up to about 3 hydroxy groups and/or the polyalkyleneoxide chain can contain up to about 10, preferably less than 5, alkylene moieties. Suitable alkyl polysaccharides are octyl, nonyldecyl, undecyldodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, and octadecyl, di-, tri-, tetra-,penta-, and hexaglucosides, galactosides, lactosides, glucoses, fructosides, fructoses and/or galactoses.

9. Polyethylene glycol (PEG) glyceryl fatty esters, as depicted by the formula $RC(O)OCH_2CH(OH)CH_2(OCH_2CH_2)_nOH$ wherein n is from about 5 to about 200, preferably from about 20 to about 100, more preferably from about 30 to about 85, and RC(0)- is an ester wherein R comprises an aliphatic radical having from about 7 to about 19 carbon atoms, preferably from about 9 to 17 carbon atoms, more preferably from about 11 to 17 carbon atoms, most preferably from about 11 to about 14 carbon atoms. The combinations of n from about 20 to about 100, with C_{12}-C_{18}, preferably C_{12}-C_{15} fatty esters, for minimized adverse effect on foaming, is preferred.

Cationic Surfactants

Cationic surfactants useful in compositions of the present invention, particularly as additional conditioner actives or as components in gel vehicles, contain amino or quaternary ammonium hydrophilic moieties which are positively charged when dissolved in the aqueous composition of the present invention. Cationic surfactants among those useful herein: are disclosed in the following documents, all incorporated by reference herein; M.C. Publishing Co., McCutcheon's Detergents & Emulsifiers, (North American edition 1979); Schwartz, et al., Surface Active Agents, Their Chemistry and Technology, New York: Interscience Publishers, 1949; U.S. Patent 3,155,591, Hilfer, issued November 3, 1964; U.S. Patent 3,929,678, Laughlin, et al., issued December 30, 1975; U.S. Patent 3,959,461, Bailey, et al., issued May 25, 1976; and U.S. Patent 4,387,090, Bolich, Jr., issued June 7, 1983.

Among the quaternary ammonium-containing cationic surfactant materials useful herein are those of the general formula:



wherein R_1-R_4 are independently and aliphatic group of from about 1 to about 22 carbon atoms, or an aromatic, alkoxy, polyoxyalkylene, alkylamido, hydroxyalkyl, aryl or alkylaryl group having from about 12 to about 22 carbon atoms; and X is an anion selected from halogen, acetate, phosphate, nitrate and alkylsulfate radicals. The aliphatic

groups may contain, in addition to carbon and hydrogen atoms, ether linkages, and other groups such as amino groups. The longer chain aliphatic groups, e.g., those of about 12 carbons, or higher, can be saturated or unsaturated.

Salts of primary, secondary and tertiary fatty amines are also suitable cationic surfactant materials. The alkyl groups of such amines preferably have from about 12 to about 22 carbon atoms, and may be substituted or unsubstituted. Such amines, useful herein, include stearamido propyl dimethyl amine, diethyl amino ethyl stearamide, dimethyl stearamine, dimethyl soyamine, soyamine, myristyl amine, tridecyl amine, ethyl stearylamine, N-tallowpropane diamine, ethoxylated (5 moles E. O.) stearylamine, dihydroxy ethyl stearylamine, and arachidylbehenylamine. Suitable amine salts include the halogen, acetate, phosphate, nitrate, citrate, lactate and alkyl sulfate salts. Such salts include stearylamine hydrochloride, soyamine chloride, stearylamine formate, N-tallowpropane diamine dichloride and stearamidopropyl dimethylamine citrate. Cationic amine surfactants included among those useful in the present invention are disclosed in U.S. Patent 4,275,055, Nachtigal, et al., issued June 23, 1981, incorporated by reference herein.

A particular category of quaternary ammonium cationic conditioning agent that can be useful herein is characterized by the formula:

$$\left[(R)_{4-m} - N^{(+)} - [(CH_2)_n - Y - R^1]_m \right] \quad X^{(-)}$$

wherein each R substituent is a short chain C_1-C_6 alkyl or hydroxyalkyl group, benzyl, or mixtures thereof; each m is 2 or 3; each n is from 1 to about 4; each Y is -O-(O)C-, or -C(O)-O-; each R^1 is a hydrocarbyl, or substituted hydrocarbyl, group, the sum of carbons in each R^1, plus one when Y is -O-(O)C-, being C_{12}-C_{22}; the average Iodine Value of the parent fatty acid of the R^1 group being from about 60 to about 140; and wherein the counterion, X^- is any compatible anion.

Zwitterionic and Amphorteric Surfactants

Zwitterionic surfactants, useful in shampoos as well as conditioners, are exemplified by those which can be broadly described as derivatives of aliphatic

quaternary ammonium, phosphonium, and sulfonium compounds, in which the aliphatic radicals can be straight or branched chain, and where one of the aliphatic substitutes contains from about 8 to about 18 carbon atoms and one contains an anionic water-solubilizing group, e.g. carboxy, sulfonate, sulfate, phosphate, or phosphonate. A general formula for these is:

$$R^2\text{-------}Y^{(+)}\text{-----}CH_2\text{-----}R^4\text{-----}Z^{(-)}$$
$$\Big|$$
$$(R^3)_x$$

wherein R^2 contains an alkyl, alkenyl, or hydroxy alkyl radical of from about 8 to about 18 carbon atoms, from 0 to about 10 ethylene oxide moieties and from 0 to about 1 glyceryl moiety; Y is selected from the group consisting of nitrogen, phosphorus, and sulfur atoms; R^3 is an alkyl or monohydroxyalkyl group containing about 1 to about 3 carbon atoms; X is 1 when Y is a sulfur atom, and 2 when Y is a nitrogen or phosphorus atom; R^4 is an alkylene or hydroxyalkylene of from about 1 to about 4 carbon atoms and Z is a radical selected from the group consisting of carboxylate, sulfonate, sulfate, phosphonate, and phosphate groups.

Other zwitterionics such as betaines are also useful in the present invention. Examples of betaines useful herein include the high alkyl betaines, such as coco dimethyl carboxymethyl betaine, lauryl dimethyl carboxymethyl betaine, lauryl dimethyl alphacarboxyethyl betaine, cetyl dimethyl carboxymethyl betaine, lauryl bis-(2-hydroxyethyl) carboxymethyl betaine, stearyl bis-(2-hydroxypropyl) carboxymethyl betaine, oleyl dimethyl gamma-carboxypropyl betaine, and lauryl bis-(2-hydroxypropyl)alpha-carboxyethyl betaine. The sulfobetaines may be represented by coco dimethyl sulfopropyl betaine, stearyl dimethyl sulfopropyl betaine, lauryl dimethyl sulfoethyl betaine, lauryl bis-(2-hydroxyethyl) sulfopropyl betaine and the like, amidobetaines and amidosulfobetaines, wherein the $RCONH(CH_2)_3$ radical is attached to the nitrogen atom of the betaine are also useful in this invention.

Examples of amphoteric surfactants which can be used in the compositions of the present invention are those which are broadly described as derivatives of aliphatic secondary and tertiary amines in which the aliphatic radical can be straight or branched chain and wherein one of the aliphatic substituents contains from about 8 to about 18

carbon atoms and one contains an anionic water solubilizing group, e.g., carboxy, sulfonate, sulfate, phosphate, or phosphonate. Examples of compounds falling within this definition are sodium 3-dodecyl-aminopropionate, sodium 3-dodeclaminopropane sulfonate, N-alkyltaurines such as the one prepared by reacting dodecylamine with sodium isethionate according to the teaching of U.S. Patent 2,658.072, N-higher alkyl aspartic acids such as those produced according to the teaching of U.S. Patent 2,438,091, and the products sold under the trade name "Miranol" and described in U.S. Patent 2,528,378 both of which patents are incorporated herein by reference.

Other surfactants that can be used include fluorosurfactants, or other halogenated surfactants, which can be anionic, nonionic cationic, amphoteric, or zwitterionic.

Fluorosufactants include perfluorinated compounds such as those represented by the formula

$$CF_3 - (CF_2)_X - (CH_2)_y - Z$$

where Z is a water solubilizing group of either organic or inorganic character, x is an integer which is generally from 2 to 17, particularly from 7 to 11, and y is and integer from 0 to 4, and said compounds may be cationic, anionic, amphoteric or zwitterionic, depending upon the nature of the grouping or groupings encompassed by Z. The Z groups may be or may comprise sulfate, sulfonate, carboxylate, amine salt, quaternary ammonium, phosphate, phosphonate, and combinations thereof. Perfluorinated compounds are also described in U.S.Patent 4,176,176, Cella et al., issued November 27, 1979, U.S. Patent 3,993,745, Cella et al., issued November 23, 1976, and U.S. Patent 3,993,744, Cella et al, issued November 23, 1976, each being incorporated herein by reference.

Fluorosurfactants, when used, will typically be used at lower levels than most other spreading agents. They will be used generally at weight ratios of polysiloxane fluid to spreading agent of from about 10,000:1 to about 1:1, preferably about 1,000:1 to about 10:1.

<u>Ethanol</u>

The compositions of the present invention will comprise from about 10% to about 50%, by weight, ethanol, preferably from about 15% to about 40%, more preferably from about 18% to about 35%, most preferably from about 20% to about 30%.

Water

The compositions of the present invention will comprise water, generally at a level of from about 30% to about 89.9%, by weight, of the composition, preferably from about 30% to about 89.8%, more preferably from about 50% to about 85%, even more preferably from about 60% to about 80%, most preferably from about 65% to about 80%.

Scalp Conditioning Agent

The compositions will preferably comprise a scalp conditioning agent which is in addition to the hair shine agent and can condition the skin of the scalp and thus reduce or eliminate any drying-out effect of the scalp. The scalp conditioning agent will preferably be present at a level of from about 0.1% to about 10%, by weight of the composition, more preferably from about 0.25% to about 5%, most preferably from about 0.5% to about 3%.

The scalp conditioning agent hereof can be any material which is suitable for conditioning skin that can provide emolliency, moisturization, or both, to the scalp and can be incorporated into the compositions hereof without preventing the compositions hereof from enhancing shine to the hair. Thus the scalp conditioning agents hereof include both skin emollients and skin humectants and combinations thereof. Emollients can include conventional lipids (e.g. esters such as fats, oils, waxes and the like), polar lipids (e.g. lipids that have been hydrophilically modified to render them more water soluble), silicones, and hydrocarbons. Scalp conditioning agents hereof will generally be nonvolatile.

Emollients

Suitable scalp conditioning agents include fatty alcohols, non-volatile hydrocarbons, low refractive index, nonvolatile polysiloxane fluids (below 1.46 refractive index) including those of the general structures represented above but characterized by lower or zero levels of aryl substitution, especially polydimethylsiloxane, and fatty esters and other lipid esters.

Fatty alcohols include C12 - C22 alcohols, preferably C16 - C18 alcohols, such as stearyl alcohol and cetyl alcohol.

Nonvolatile hydrocarbon oils include linear, and branched chain hydrocarbons, including saturated and unsaturated hydrocarbons. The hydrocarbon oils include, but are not limited to, straight chain hydrocarbons with 12 - 20 carbon atoms, branched chain

hydrocarbons with 12 carbon atoms and higher, polymeric hydrocarbons of alkenyl monomers, such as C2 - C6 alkenyls, which can be straight or branched chains (typically with weight average molecular weight up to about 500, though higher levels are not excluded). Specific examples of ther hydrocarbon materials include paraffin oil, mineral oil, saturated or unsaturated dodecane, tetradecane, pentadecane, and hexadecane, and polybutene.

Fatty esters include esters derived from fatty alcohols or fatty acids (such as but not limited to those having C12- C22 carbon atoms), such as but not limited to mono- di-, and tri-carboxylic esters. The hydrocarbyl radicals of the fatty esters and alcohols can also be subsitituted with other functional groups, such as amides and alkoxy moities (e.g., ethoxy or ether linkages).

Mono-carboxylic acid esters include those of the formula R'OOR wherein R and R' are unsubstituted or substituted alkyl or alkenyl radicals wherein the sum of carbon atoms in R and R' is at least ten, preferably at least 20. Examples include fatty esters such as alkyl and alkenyl esters of fatty acids having C10 - C22 carbon chains and alkyl and alkenyl fatty alcohol carboxylic acid esters having and alcohol-derived chain of from about 10-22 carbon atoms. Preferred are C10-C22 esters having C6 - C22 R groups. Examples include esters such as stearates, isostearates, laurates, palmitates, oleates, adipates, lactates, myristates, acetates, and propionates having hexyl, isohexyl, decyl, isodecyl, hexadecyl, cetyl, lauryl, myristyl, or oleyl. Examples of other suitable, esters include diisopropyl adipate, diisohexyl adipate, and diisopropyl sebacate.

Di- and tri- alkyl and alkenyl esters of carboxylic acids include, for example, C1 - C22, preferably C1 - C6, esters of C4 - C8 di- or tri-carboxylic acids such as succinic acid, glutaric acid, adipic acid, hexanoic acid, heptanoic acid, and octonoic acid, e.g., isocetyl stearoyl stearate, diisoproply adipate, and tristearyl citrate.

Polyhydric alcohol esters include alkylene glycol fatty acid esters, for example ethylene glycol mono- and di-fatty acid esters, diethylene glycol mono-and di-fatty acid esters, polyethylene glycol mono- and di- fatty acid esters, and propylene glycol mono- and di-fatty acid esters. Examples include polypropylene glycol monooleate or monostearate, ethoxylated propylene glycol monostearate, glyceryl mono- and di- fatty acid esters, polyglycerol poly-fatty acid esters, ethoxylkated glyceryl monostearate, 1,3-butylene glycol distearate, polyoxyethylene polyol fatty acid ester, sorbitan fatty acid

esters, and polyoxyethylene sorbitan fatty acid esters. Another suitable material is glycerol monostearate.

Glycerides include mono-, di-, and tri-glycerides, including such mono-, di-, and tri-esters of glycerol and long chain carboxylic acids such as C10-C22 carboxylic acids. These types of materials can be obtained from vegetable and animal fats and oils such as castor oil, safflower oil, lanolin, and the like. Synthetic oils include triolein and tristearin glyceryl dilaurate.

Polyol carboxylic acid ester are also useful emollients for use herein. These polyol carboxylic acid esters are generally derived from a polyol radical or moiety and one or more carboxylic acid radicals or moieties. In other words, these esters contain a moiety derived from a polyol and one or more moieties derived from a carboxylic acid. These polyol carboxylic acid esters can also be described as polyol fatty acid esters, because the terms carboxylic acid and fatty acid are often used interchangeably by those skilled in the art.

The preferred polyol carboxylic acid polyesters employed in this invention comprise certain polyols, especially sugars or sugar alcohols, esterified with at least four fatty acid groups. Accordingly, the polyol starting material must have at least four esterifiable hydroxyl groups. Examples of preferred polyols are sugars, including monosaccharaides and disaccharides, and sugar alcohols. Examples of monosaccharides containing four hydroxyl groups are xylose and arabinose and the sugar alcohol derived from xylose, which has five hydroxyl groups, i.e., xylitol. The monosaccharide, erythrose, is not suitable in the practice of this invention since it only contains three hydroxyl groups, but the sugar alcohol derived from erythrose, i.e., erythritol, contains four hydroxyl groups and accordingly can be used. Suitable five hydroxyl group-containing monosaccharides are galactose, fructose, and sorbose. Sugar alcohols containing six -OH groups derived from the hydrolysis products of sucrose, as well as glucose and sorbose, e.g., sorbitol, are also suitable. Examples of disaccharide polyols which can be used include maltose, lactose, and sucrose, all of which contain eight hydroxyl groups.

Preferred polyols for preparing the polyesters for use in the present invention are selected from the group consisting of erythritol, xylitol, sorbitol, glucose, and sucrose. Sucrose is especially preferred.

The polyol starting material having at least four hydroxyl groups is esterified on at least four of the -OH groups with a fatty acid containing from about 8 to about 22 carbon atoms. Examples of such fatty acids include caprylic, capric, lauric, myristic, myristoleic, palmitic, palmitoleic, stearic, oleic, ricinoleic, linoleic, linolenic, eleostearic, arachidic, arachidonic, behenic, and erucic acid. The fatty acids can be derived from naturally occurring or synthetic fatty acids; they can be saturated or unsaturated, including positional and geometrical isomers. However, in order to provide liquid polyesters preferred for use herein, at least about 50% by weight of the fatty acid incorporated into the polyester molecule should be unsaturated. Oleic and linoleic acids, and mixtures thereof, are especially preferred.

The polyol carboxylic acid esters useful in this invention should contain at least four fatty acid ester groups. It is not necessary that all of the hydroxyl groups of the polyol be esterified with fatty acid, but it is preferable that the polyester contain no more than two unesterified hydroxyl groups. Most preferably, substantially all of the hydroxyl groups of the polyol are esterified with fatty acid, i.e., the polyol moiety is substantially completely esterified. The fatty acids esterified to the polyol molecule can be the same or mixed, but, a substantial amount of the unsaturated acid ester groups should preferably be present to provide liquidity.

The following are non-limiting examples of specific polyol carboxylic acid esters containing at least four fatty acid ester groups suitable for use in the present invention: glucose tetraoleate, the glucose tetraesters of soybean oil fatty acids (unsaturated), the mannose tetraesters of mixed soybean oil fatty acids, the galactose tetraesters of oleic acid, the arabinose tetraesters of linoleic acid, xylose tetralinoleate, galactose pentaoleate, sorbitol tetraoleate, the sorbitol hexaesters of unsaturated soybean oil fatty acids, xylitol pentaoleate, sucrose tetraoleate, sucrose pentaoletate, sucrose hexaoleate, sucrose hepatoleate, sucrose octaoleate, and mixtures thereof.

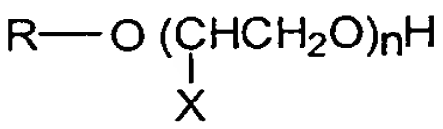
As noted above, highly preferred polyol carboxylic acid esters are those wherein the fatty acids contain from about 14 to about 18 carbon atoms.

The preferred polyol carboxylic acid esters for use herein are liquids, and have complete melting points below about 30^{o}C, preferably below about 27.5^{o}C, more

preferably below about 25°C. Complete melting points reported herein are measured by Differential Scanning Calorimetry (DSC).

Polyol fatty acid polyesters suitable for use herein can be prepared by a variety of methods well known to those skilled in the art. These methods include: transesterification of the polyol with methyl, ethyl or glycerol fatty acid esters using a variety of catalysts; acylation of the polyol with a fatty acid chloride; acylation of the polyol with a fatty acid anhydride; and acylation of the polyol with a fatty acid, per se. See U.S. Patent No. 2,831,854; U.S. Patent No. 4,005,196, to Jandacek, issued January 25, 1977; U.S. Patent No. 4,005,196, to Jandacek, issued January 25, 1977.

Alkoxylated alcohols useful herein can be described by the following general formula:



wherein R is selected from the group consisting of alcohols, polyols, diols, and mixtures thereof, having a chainlength of from about 2 to about 30 carbon atoms; n is an integer from about 3 to about 40; X is selected from the group consisting of hydrogen, methyl, ethyl, propyl, and mixtures thereof.

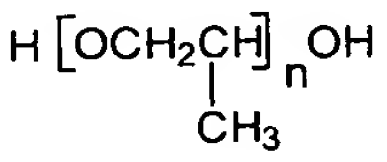
Preferably R is selected from the group consisting of alcohols, polyols, diols, or mixtures thereof, having a chainlength of from about 4 to about 20 carbon atoms; X is methyl; and n is an integer from about 6 to about 35. More preferably R is selected from the group consisting of alcohols, polyols, diols, or mixtures thereof, having a chainlength of from about 4 to about 18 carbon atoms; X is methyl; and n is an integer from about 10 to about 20.

Nonlimiting examples of classes of alkoxylated alcohols useful herein include propoxylated and butoxylated ethers of alcohols and polyols. These compounds can be described as PPG and PBG alkyl ethers wherein the PPG and PBG are commonly used designations for polypropylene glycol and polybutylene glycol, respectively. The average number of PPG or PBG groups in these ethers is commonly given by a number designation after the PPG or PBG. For example, PPG-14 butyl ether, would designate a polypropylene glycol ether of butanol wherein the molecule has on average 14 propylene glycol units.

Nonlimiting examples of alkoxylated alcohols useful herein include PPG-10 butyl ether, PPG-11 butyl ether, PPG-12 butyl ether, PPG-13 butyl ether, PPG-14 butyl ether, PPG-15 butyl ether, PPG-16 butyl ether, PPG-17 butyl ether, PPG-18 butyl ether, PPG-19 butyl ether, PPG-20 butyl ether, PPG-22 butyl ether, PPG-24 butyl ether, PPG-30 butyl ether, PPG-11 stearyl ether, PPG-15 stearyl ether, PPG-10 oleyl ether, PPG-7 lauryl ether, PPG-30 isocetyl ether, PPG-10 glyceryl ether, PPG-15 glyceryl ether, PPG-10 butyleneglycol ether, PPG-15 butylene glycol ether, PPG-27 glyceryl ether, PPG-30 cetyl ether, PPG-28 cetyl ether, PPG-10 cetyl ether, PPG-10 hexylene glycol ether, PPG-15 hexylene glycol ether, PPG-10 1,2,6-hexanetriol ether, PPG-15 1,2,6-hexanetriol ether, and mixtures thereof.

Nonlimiting examples of alkoxylated polyols useful herein include those selected from the group consisting of PPG-10 1,4-butanediol, PPG-12 1,4-butanediol, PPG-14 1,4-butanediol, PPG-2 butanediol, PPG-10 1,6-hexanediol, PPG-12 1,6-hexanediol, PPG-14 hexanediol, PPG-20 hexanediol, and mixtures thereof. Preferred are those selected from the group consisting of PPG-10 1,4-butanediol, PPG-12 1,4-butanediol, PPG-10 1,6-hexandiol, and PPG-12 hexanediol, and mixtures thereof.

Polypropylene glycols are also suitable emollients for use herein. They can be described as polymers which are typically formed from the polymerization of propylene oxide, propylene glycol, propylchlorohydrin, propylbromohydrin, and other related materials. Preferred polypropylene glycols are represented by the following formula:



wherein n is an integer from about 10 to about 50, preferably from about 15 to about 40, and more preferably from about 20 to about 34. In the above structure, even though one isomeric orientation is depicted for convenience, this depiction is not intended to preclude other isomeric structures. The polypropylene glycols are commonly designated as PPG's followed by a number indicating the average number of repeating units in the structure. For example, PPG-30 would correspond to the above structure wherein n has an average value of about 30. Based on this nomenclature, the polypropylene glycols useful herein encompass those designated as PPG-10 through PPG-50, more preferably those

designated as PPG-15 through PPG-40, and most preferably those designated as PPG-20 through PPG-34.

Humectants

Humectants can also possess moisturizing properties for the scalp. Examples of humectants useful herein include materials such as urea; guanidine; saturated or unsaturated alkyl alpha hydroxy acids such as glycolic acid and glycolate salts (e.g. ammonium and quaternary alkyl ammonium) and lactic acid and lactate salts (e.g. ammonium and quaternary alkyl ammonium); aloe vera in any of its variety of forms (e.g. aloe vera gel); polyhydroxy alcohols such as sorbitol, glycerol, low molecular weight polypropylene glycols (e.g., dipropylene glycol and tripropylene glycol), hexanetriol, propylene glycol, butylene glycol, hexylene glycol, and the like; polyethylene glycol; sugars and starches; sugar and starch derivatives (e.g., alkoxylated glucose); hyaluronic acid; chitin, starch-grafted sodium polyacrylates such as Sanwet (RTM) IM-1000, IM-1500, and IM-2500 (available from Celanese Superabsorbent Materials, Portsmouth, VA); lactamide monoethanolamine; acetamide monoethanolamine; propoxylated glycerol (as described in U.S. Patent No. 4,976,953 to Orr et al., issued December 11,1990, which is incorporated by reference herein in its entirety); and mixtures thereof.

Humectants useful in the compositions of the present invention include C3-C6 diols and triols, and propoxylated glycerin. Examples include propylene glycol, 1,3-dihydroxypropane, glycerin, butylene glycol, hexylene glycol, 1,4-dihydroxyhexane, 1,2,6-hexanetriol, dipropylene glycol, tripropylene glycol, and mixtures thereof. Humectants also include water-soluble polyglycerylmethacrylates such as Lubrajels TM, (Guardian Chemical Corp., Hauppage, NY, USA). Lubrajels are hydrates or cathrates formed by the reaction of sodium glycerate with a methacrylic polymer.

Other Ingredients

The compositions hereof can also contain other ingredients suitable for use as carriers or vehicles for the composition, as well as other active ingredients in addition to the essential active ingredients discussed above.

Choice of appropriate additional carrier ingredients will depend on the particular polysiloxane fluid to be used, and the particular type of composition that is desired. The choice and formulation of such products is well within the ambit of those of ordinary skill in the art.

Nonlimiting, exemplary additional ingredients are further described below.

Suitable additional carrier fluids for use in the present invention include, but are not limited to lower alcohols such as isopropanol, hydrocarbons (such as isobutane, hexane, decene, acetone), halogenated hydrocarbons (such as Freon), linalool, hydrocarbon esters (such as ethyl acetate, dibutyl phthalate), volatile silicone derivatives, especially siloxanes, such as cyclomethicone and dimethicone (having for example, viscosity at 25°C of about 15 centipoise or less), and mixtures thereof.

The composition may include gel vehicle materials. The gel vehicle can comprise two components: a lipid vehicle material and a cationic surfactant vehicle material. Cationic surfactant materials are described in detail above. Preferred cationic surfactants are quaternary ammonium compounds such as ditallow dimethyl ammonium salts. Another preferred type of quaternary ammmonium compounds are the tri-short chain alkyl (C1 - C3, preferably C1) mono-long chain alkyl (C10- C22, preferably C16-C18, especially cetyl) ammonium salts. Preferred counter-ions are sulfates and chorides, especially chloride. Gel vehicles are generally described in the following documents, all incorporated by reference herein: Barry, "The Self Bodying Action of the Mixed Emulsifier Sodium Dodecyl Sulfate/Cetyl Alcohol", 28 J. of Colloid and Interface Science 82091 (1968), Barry et al, "The Self-Bodying Action of Alkyltrimethyl-ammonium Bromides/Cetostearyl Alcohol Mixed Emulsifiers, Influence of Quaternary Chain Length", 35 J of Colloid and Interface Science 689-708 (1971); and Barry et al. "Rheology of Systems Containing Cetomacrogol 1000- Cetostearyl Alcohol, I. Self Bodying Action", 38 J of Colloid and Interface Science 616-625 (1972). Lipid vehicle materials which are essentially water-insoluble, and contain hydrophobic and hydrophilic moieties and include naturally or synthetically-derived acids, acid derivatives, alcohols, esters, ethers, ketones, and amides with carbon chains of from about 12 to about 22, preferably from about 16 to about 18, carbon atoms in length. Such materials also act as emollients, a wide variety of which are described above. Fatty alcohols and fatty esters are preferred. Fatty alcohols are particularly preferred. Exemplary ester lipids for forming gel vehicles are cetyl palmitate and glycerylmonostearate.

If a gel vehicle formed from cationic surfactant and lipid vehicle material is used in the compositions of the present invention, the lipid vehicle material is preferably present at from about 0.1% to about 10.0% of the composition; the cationic surfactant

vehicle material is preferable present at from about 0.2% to about 5.0% of the composition.

Other gelling agents can also be used in the present invention. Without limitation these include hydrophilic polymers such as: acrylic acid/acrylates cross polymers such as carbomers marketed by B.F.Goodrich under the Carbopol ™ tradename; cellulose ethers, such as hydroxy ethyl cellulose, methyl cellulose, and hydroxypropyl cellulose; polyvinylpyrrolidone; polyvinylalcohol, guar gum, hydroxypropyl guar gum, xanthan gum, and other water soluble, water/ethanol soluble, or colloidally soluble polymers. Such gelling agents are generally used at levels of from about 0.1% to about 5%, preferably from about 0.5% to about 2%, by weight of the composition.

Alternately, other materials can be used to impart a gel-like viscosity to the composition, such as thickeners (e.g., clays), viscosity modifiers, etc. Mixtures of these materials can also be used.

Suspending agents may also be utilized as carrier components for suspending the polysiloxane fluid/spreading agent hair shine agent and/or other immiscible or particulate ingredients (e.g. anti-static cationic surfactants which are insoluble in the composition, anti-dandruff actives such as zinc pyrithione (ZPT), sulfur, selenium sulfide, coal tar, piroctone olamine, ketoconazole, climbazole, salicylic acid, etc. A suspending agent can be particularly important in pourable liquid formulations. A preferred suspending agent is a crystalline long chain acyl deriviative such as ethylene glycol distearate, as described with other suitable ethylene glycol esters of fatty acids with from 16 - 22 carbon atoms in US Patent 4,741,855, Grote, Russell, Procter & Gamble, incorporated herein by reference.

The compositions hereof may also utilize an emulsifying agent. Emulsifying agents can be used to assist with stable dispersion of the hair shine agent, particularly in low viscosity compositions such as hair tonics. They can also be used to form emulsified creams. Suitable emulsifying agents include nonionic, cationic, anionic surfactants, or mixtures thereof. Examples of a variety of surfactants suitable for use as emulsifying agents are included in the discussion of surfactants above, particularly the nonionic surfactants and _cationic surfactants as described above. Such emulsified creams can comprise an emulsifying agent in combination with a hydrocarbon, lipid or lipid vehicle material such as those disclosed above. If an emulsifying agent is used, it is preferably present at a level of from about 0.01% to about 7.5% of the composition.

The compositions hereof may contain additional hair conditioning ingredients, such as but not limited to cationic surfactants, cationic polymers as additional hair conditioning ingredients, and other hair conditioning ingredients such as panthenol, panthetine, pantotheine, panthenyl ethyl ether, and combinations thereof.

Suitable cationic polymers include, for example, copolymers of vinyl monomers having cationic amine or quaternary ammonium functionalities with water soluble spacer monomers such as acrylamide, methacrylamide, alkyl and dialkyl acrylamides, alkyl and dialkyl methacrylamides, alkyl acrylate, alkyl methacrylate, vinyl caprolactone, and vinyl pyrrolidone. The alkyl and dialkyl substituted monomers preferably having C_1-C_7 alkyl groups, more preferably C_1-C_3 alkyl groups. Other suitable spacer monomers include vinyl esters, vinyl alcohol (made by hydrolysis of polyvinyl acetate), maleic anhydride, propylene glycol and ethylene glycol. Other cationic polymers include cationic-modified polysaccharide, such as cationic ammonium modified cellulose.

Especially preferred are cationic saccharide polymers (including copolymers) of saccharide having a cationic charge density of greater than about 1.2meq/g, preferably greater than about 1.5 meq/g, more preferably greater than about 1.7meq/g, even more preferably greater than about 1.8meq/g. Generally the cationic polymers will have a cationic charge density of less than about 5meq/g, preferably less than about 3.5meq/g, more preferably less than about 2.5meq/g, even more preferably less than about 2.2meq/g.

The "cationic charge density" of a polymer refers to the ratio of the number of positive charges on a monomeric unit of which the polymer is comprised to the molecular weight of said monomeric unit, i.e.:

$$\text{Cationic Charge Density} = \frac{\text{number of positive charges}}{\text{monomeric unit molecular weight}}$$

The cationic charge density of the cationic polymers herein can be determined using the Kjeldahl Method (United States Pharmacopoeia - Chemical tests - <461> Nitrogen Determination - method II). Cationic charge density is determined at the pH of the particular product in which the polymer is used, and preferably meets the above limitations at such pH.

Such cationic saccharides polymers generally will comprise from about 1% to about 10%, preferably from about 2% to about 5%, more preferably from about 2.3% to about 3%, even more preferably from about 2.5% to about 2.9%, by weight, of cationic nitrogen.

The cationic saccharides for use herein will generally have an average molecular weight of from about 5000 to about 10 million, preferably from about 100,000 to about 5 million, more preferably from about 500,000 to about 2 million, even more preferably from about 1 million to about 1.5 million.

Cationic polysaccharide polymers include the following non-limiting examples: cationic celluloses and hydroxyethylcelluloses, cationic starches and hydroxyethylstarches. Non-limiting examples of suitable cationic polymers are those available from Amerchol Corp. (Edison, NJ, USA) as salts of hydroxyethyl cellulose reacted with trimethyl ammonium substituted epoxide, referred to in the industry (CTFA) as Polyquaternium 10.

Suitable cationic surfactants are generally described above.

The compositions hereof can also contain film forming polymers, i.e. adhesive polymers.

Exemplary adhesive polymers include polyvinylpyrrolidone (PVP), particularly poly N-vinyl pyrrolidone, copolymers of PVP and methylmetharylate, copolymers of PVP and vinyl acetate (VA), and polyvinyl alcohol (PVA).

Exemplary adhesive polymers also include copolymers of VA and crotonic acid, copolymers of methylvinylether and maleic hemiesters (e.g. maleic ethyl ester and maleic butyl ester), hydroxypropyl cellulose, hydroxypropyl guar gum, polystyrene sulfonate salts, polyacrylic polymers such as polymers and copolymers of acrylic acid and methacrylic acid, co- and ter-polymers of acrylic acid and/or methacylic acid with acrylamide and/or vinyl pyrrolidone such as terpolymers of vinyl pyrrolidone/methyl methacrylate/methacrylic, terpolymers of vinyl pyrrolidone/ethylmethacrylate/ methacrylic acid, terpolymers of t-butyl acrylamide/ethyl acrylate/acrylic acid, and terpolymers of VA/crotonic acid/vinyl neodecanoate.

Other examples of anionic hair hold polymers are crotonic acid and a vinyl ester of an alpha-branched saturated aliphatic monocarboxylic acid such as vinyl neodecanoatel and copolymers of methyl vinyl ether and maleic anhydride (e.g. molar ratio about 1:1)

wherein such copolymers are 50% esterfied with a saturated aliphatic alcohol containing from 1 to 4 carbon atoms such as ethanol or butanol; and acrylic copolymers and terpolymers containg acrylic acid or methacrylic acid as the anionic radical-containing moiety such as copolymers with, butyl acrylate, ethyl methacrylate, etc.

Polymeric hair hold polymers also include amphoteric polymers. One class of amphoteric polymers that can be used are acrylic resins with both cationic and carboxylic groups. Examples include terpolymers of octyl and acrylamide/acrylic acid/butylaminoethyl methacrylate, copolymers of acrylic acid/betaine methacrylate, and copolymers of octylacrylamide/acrylates.

Also silicone grafted adhesive copolymers can be used, such as those described in which are polysiloxane-containing monomers with non-polysiloxane-containing monomers such that said adhesive agent has a weight average molecular weight of at least about 20,000, and comprises from about 1% to about 50%, by weight, of the polysiloxane-containing monomers.

Suitable film-forming polymers also include silicone-containing adhesive polymers. A preferred polymer of this type comprises an organic backbone, especially a carbon backbone such as a vinyl polymeric backbone, and also preferably, a polydimethylsiloxane macromer having a weight average molecular weight of at least about 500, preferably from about 1,000 to about 100,000, more preferably from about 2,000 to about 50,000, most preferably about 5,000 to about 20,000, is grafted to the backbone. Organic backbones contemplated include those that are derived from polymerizable, ethylenically unsaturated monomers. These include vinyl monomers, and other condensation monomers (e.g., those that polymerize to form polyamides and polyesters) and ring-opening monomers (e.g. ethyl oxazoline and caprolactone).

The preferred polymerizable polysiloxane-containing monomer (C monomer) can be exemplified by the general formula:

$$X(Y)_nSi^R_{3-m}Z_m$$

wherein X is a vinyl group copolymerizable with the A and B monomers; Y is a divalent linking group; R is a hydrogen, hydroxyl, lower alkyl (e.g. C_1-C_4) aryl, alkaryl, alkoxy, or alkylamino; Z is a monovalent siloxane polymeric moiety having a number average

molecular weight of a least about 500, is essentially unreactive under copolymerization conditions, and is pendant from the vinyl polymeric backbone described above; n is 0 or 1; and m is an integer from 1 to 3.

Examples of useful polymers and how they are made are described in detail in U.S. Patent 4,693,935, Mazurek, issued September 15, 1987, U.S. Patent 4,728,571, Clemens et al., issued March 1, 1988 both of which are incorporated herein by reference.

Suitable polymers are also disclosed in EPO Application 90307528.1, published as EPO Application 0 408 311 A2 on January 11, 1991, Hayama, et al., U.S. Patent 5,061,481, issued October 29, 1991 Suzuki et al., U.S. Patent 5,106,609, Bolich et al., issued April 21, 1992, U.S. Patent 5,100,658, Bolich et al., issued March 31, 1992, U.S. Patent 5,100,657, Ansher-Jackson, et al., issued March 31, 1992, U.S. Patent 5,104,646, Bolich et al., issued April 14, 1992 and U.S. Serial No. 08/104,232, Bolich et al, filed August 10, 1993 all of which are incorporated by reference herein. Preferred of these polymers are copolymers comprising t-butyl acrylate and/or t-butyl methacrylate with vinyl monomers having polydimethylsiloxane macromers covalently attached thereto.

The compositions herein can contain a variety of other optional components suitable for rendering such compositions more cosmetically or aesthetically acceptable or to provide them with additional usage benefits. Such conventional optional ingredients are well-know to those skilled in the art, e.g., opacifiers such as polystyrene; pearlescent aids, such as ethylene glycol distearate (which is also a suspending agent and can be used to suspend insoluble materials in the compositions), mica, and mother of pearl; preservatives, such as benzyl alcohol, methyl paraben, propyl paraben and imidazolidinyl urea; thickeners and viscosity modifiers, such as a diethanolamide of a long chain fatty acid (e.g., PEG 3 lauric diethanolamide), cocomonoethanol amide, starches and starch derivatives;; sodium chloride; sodium sulfate; polyvinyl alcohol;; pH adjusting agents such as citric acid, sodium citrate, succinic acid, phosphoric acid, sodium hydroxide, sodium carbonate; salts, in general, such as potassium acetate and sodium chloride; coloring agents, such as any of the FD&C or D&C dyes; hair oxidizing (bleaching) agents, such as hydrogen peroxide, perborate and persulfate salts; hair reducing agents, such as the thioglycolates; hair dyes; perfumes; sequestering agents, such as tetrasodium ethylenediamine tetra-acetate; sensates such as those that chemically stimulate the nerve endings to induce a perception of cooling, heat, or other sensation of change in conditions when applied to the skin, e.g.,

camphor, menthol, l-isopulegol, ethyl menthane carboxamide and trimethyl isopropyl butanamide, and others including but not limited to those disclosed in GB-B-1315626, GB-B-1404596 and GB-B-1411785, all incorporated by reference; anti-dandruff agents such as zinc pyrithione, piroctone olamine, ketoconazole, climbazole, salicylic acid; antioxidants/ ultra violet filtering agents such as octyl methoxycinnamate, benzophenone-3 and DL-alpha tocopherol acetate and polymer plasticizing agents, such as glycerin, disobutyl adipate, butyl stearate, and propylene glycol. Such optional ingredients generally are used individually at levels of from about 0.01% to about 10.0%, preferably from about 0.05% to about 5.0%, of the composition.

The pH of the present compositions generally will be between about 3 and about 9, preferably between about 4 and about 8.

As with all compositions, the present invention should not contain components which unduly interfere with the performance of the compositions.

The hair care compositions of the present invention can be made using conventional formulation and mixing techniques. Exemplary methods of making various types of cosmetic compositions are also described more specifically in the Examples below.

Any of a variety of conventional packages for the hair care products can be used, as is previously discussed. Selection of spray packages, including aerosols and nonaerosols, which will provide the required particle size distribution for sprays in accordance with the present invention is well within the ambit of one of ordinary skill in the hair spray art. Aerosol hair sprays additionally utilize a propellant which can be intermixed with the composition itself or be separately incorporated into the package. Examples of propellants include, but are not limited to trichlorofluoromethane, dichlorodifluoromethane, difluoroethane, dimethylether, propane, n-butane or isobutane. The level of propellant can be adjusted as desired but is generally used at a level of from about 5% to about 50%, by weight, of the aerosol hair spray compositions.

Suitable spray containers are well known in the art and include conventional, non-aerosol pump sprays i.e. "atomizers", aerosol containers or can having propellant, as described above, and also pump aerosol containers utilizing compressed air as the propellent. Pump aerosol containers are disclosed, for example, in U.S. Patents 4,077,441, March 7, 1978, Olofsson and 4,850,577, July 25, 1989, TerStege, both

incorporated by reference herein, and also in U.S. Serial No. 07/839,648, Gosselin, Lund, Sojka, and Lefebvre, filed February 21, 1992, "Consumer Product Package Incorporating A Spray Device Utilizing Large Diameter Bubbles".

Method of Use

The hair care compositions of the present invention can be applied to the hair and scalp in conventional ways to provide shine, conditioning, and the clean feel and refreshment benefits of the present invention. Such method of use depends upon the type of composition employed but generally involves application of an effective amount of the product to the hair or scalp, working the product throughout the hair and scalp, or to selected portions thereof, with the hands or with a hair care implement suitable for applying and/or distributing the composition, such as a comb, brush, nozzle, sponge, or other device. The hair is then preferably manipulated to the desired style or design desired by the user or hair stylist. In the preferred embodiment the composition is a leave-on product and the composition is then allowed to remain on the hair to dry, without rinsing. The hair sprays which contain adhesive hair setting polymers, however, are generally used by spraying the composition onto hair which has already been manipulated to the desired style, and then allowing the composition to dry without rinsing. By "effective amount" is meant an amount sufficient to provide a hair shine benefit. The compositions can be applied to either wet or dry hair. As used herein, wet hair also includes damp hair. Generally from about 4 g to about 20 g of the composition is applied to the hair and scalp, however these amounts can vary by preference of the user or for selected applications, such as those limited to specific portions of the hair and scalp.

Experimental

The following procedure is used to determine Glossmeter Specular Reflectance.

A collagen solution is prepared by dissolving 10.0g of gelatin (175 bloom) in 83.0 g DRO (double reverse osmosis) water at 68°C, with stirring. Next, 0.05g propylparaben is dissolved in the gelatin solution. Next, 4.5g 1M N_aOH is added, followed by 3.0g of Ceraphyl GA-D (a mixture of 10-15% soy bean oil and 85-90% maleated soy bean oil available from VanDyk Inc., Belleville, NJ, USA) to form a stable, white emulsion. Next, 1.2g of lactic acid is stirred into the emulsion, referred hereinafter as Solution A.

A 3.0%, by weight, formaldehyde in water solution, Solution B, is prepared and contained separately from Solution A.

Ceramic tiles, approximately 7.3cm x 7.3cm in size having a black glazed top and an average peak height ("roughness") of 5.0-7.0 microns (can be measured with a Rodenstock RM600-2D/3-D Measuring Station (Rodenstock Meterology, Munich, W. Germany)) are prepared and coated with the collagen on their top surfaces. Glossmeter Specular Reflectance of the collagen-coated tile should be from 8.0 - 12.0%.

Specular reflectance of the collagen-coated tile is measured utilizing a glossmeter, such as a BYK-Gardner "micro-gloss" glossmeter. Specular reflection measurements are made as described in ASTM Method D 523 at an angle of incidence of 60°. Specular reflectance as measured this is referred to herein as "Glossmeter Specular Reflectance". The tiles can be prepared as follows. Syringe A is filled with 3.0cc of Solution A. Syringe B is filled with 0.2cc of solution B. Syringe B contents are emptied onto the top surface of a tile. Syringe A contents are emptied onto the top of Solution B, on the top surface of the tile. The solutions are mixed for five seconds and spread uniformly on the top surface of the tile with a spatula. At 30 seconds after mixing, a 1.0 inch inside diameter metal ring is placed on the top surface of the tile. The collagen film is allowed to dry for eight hours. The metal ring is removed. The roughness of the collagen coated surface of the tile should be from 3.0 to 5.0 microns.

Polysiloxane and spreading agent mixtures are prepared, as described above, at a 1.00% concentration in a compatible diluent at a weight ratio of said polysiloxane fluid to said spreading agent corresponding to that found in the composition. A syringe is used to deposit 0.05cc of the mixture at the center of the area encompassed by the ring on the surface of the collagen-coated tile the mixture is allowed to dry. Glossmeter Specular Reflectance is measured.

Examples

The following examples further illustrate preferred embodiments within the scope of the present invention. The examples are given solely for the purposes of illustration and are not to be construed as limitations of the present invention as many variations of the invention are possible without departing from its spirit and scope.

PREMIX EXAMPLES 1-6

The following are a variety of exemplary polysiloxane fluid/spreading agent mixtures useful in the present invention. The mixtures can be used directly for treatment of the hair or, more preferably, can be used as components in a variety hair care compositions containing other cosmetically or pharmaceutically active ingredients, carrier ingredients, or other ingredients.

Component (Weight%)	Ex.1	Ex.2	Ex.3
Pentaphenyl Trimethyl Trisiloxane(1)	57.00	0.00	50.00
Methylphenyl Diphenyl Siloxane Copolymer (2)	38.00	0.00	0.00
Diphenyl Dimethyl Siloxane Copolymer (3)	0.00	45.00	0.00
Dimethicone (4)	0.00	50.00	0.00
MQ Silicone Resin/Volatile Cyclomethicone(5)	5.00	5.00	0.00
Dimethicone Copolyol (6)	0.00	0.00	50.00
Fluorosurfactant (7)	0.00	1.00	0.00
Cyclomethicone (8)	0.00	0.00	0.00

Component (Weight%)	Ex.4	Ex.5	Ex.6
Pentaphenyl Trimethyl Trisiloxane(1)	99.00	15.00	27.00
Methylphenyl Diphenyl Siloxane Copolymer (2)	0.00	0.00	12.00
Diphenyl Dimethyl Siloxane Copolymer (3)	0.00	0.00	0.00
Dimethicone (4)	0.00	0.00	0.00
MQ Silicone Resin/Volatile Cyclomethicone(5)	0.00	5.00	5.00
Dimethicone Copolyol (6)	0.00	0.00	0.00
Fluorosurfactant (7)	1.00	0.00	1.00
Cyclomethicone (8)	0.00	80.00	0.00

1. Dow Corning 705, Dow Corning
2. PS162, Huls
3. SF1265, General Electric
4. SE76, General Electric
5. SS4320, General Electric (50%/50% of polytrimethyl hydrosilylsilicate/ decamethylcyclopentasiloxane)
6. Dow Corning 190, Dow Corning

7. FC-171 Fluorad, 3M
8. Dow Corning 344, Dow Corning

The premix is prepared by blending all the ingredients with agitation for about ½ hour at room temperature.

The following exemplary hair care compositions can be made utilizing any of the polysiloxane fluid/spreading agent premix Examples 1-6, above (hereafter referred to as "Silicone Premix Examples).

EXAMPLES I-III

The following are leave-on hair treatment compositions representative of the present invention.

Component	Example 3(Weight%)		
	I	II	III
Silicone Premix	4.5	4.5	4.5
Ethanol	10.0	50.0	25.0
Diisobutyl adipate	0.7	--	--
Potassium Hydroxide Solution (45% conc)	1.0	1.0	1.0
Perfume	0.2	0.2	0.2
Water	----------q.s to 100%----------		

This product is prepared by dissolving the silicone premix to the ethanol and mixing for several hours until all of the premix is dissolved. Plasticizer is then added if applicable. Potassium hydroxide is then added. Water or water/surfactant, as applicable is added. Fragrance is added last. All ingredients are added under mixing conditions. The product can be applied as a tonic or sprayed from an aerosol or nonaerosol spray container that provides a particle size distribution of at least 40% of the particles having particle size of at least 100 microns..

EXAMPLE IV

The following is a hair grooming tonic composition representative of the present invention.

Component	Weight %
Silicone Premix	0.70

Perfume	0.10
Ethanol	25.0
PEG 60 Hydrogenated Castor Oil	0.60
Water	q.s.

The composition is made by mixing the above components together in a conventional manner.

EXAMPLE V

The following is a styling gel composition representative of the present invention.

Component	Weight %
Silicone Premix	2.00
Carbopol 940[1]	0.75
Triethanolamine	1.00
Dye solution	0.05
Perfume	0.10
Laureth-23	0.10
Ethanol	20.00
DRO H_2O	q.s.

1 cross-linked polyacrylic acid, commercially available from B.F.Goodrich.

This batch is made by mixing the listed components together in a conventional manner.

EXAMPLE VI

A hair tonic composition of the present invention is prepared as follows:

Component	Weight %
Silicone Premix	4.00
Water	61.000
Ethanol	35.000

All of the ingredients are mixed together at ambient temperature until the polymer is dissolved.

EXAMPLES VII-VIII

Ingredient (wt. %)	VII (Spray)	VIII (Gel)	
Carbopol Ultrez 10[1]	-	0.50	A
Carbopol 934[2]	-	-	A
Polyquaternium 10[3]	0.075	-	A
trisodium citrate	0.70	0.10	A
Ethanol (denatured)	25.00	20.00	B
l-isopulegol[4]	-	0.20	B
PEG 60 hydrogenated castor oil[5]	0.80	0.10	B
lactic acid	0.10	0.02	B
phenoxyethanol	0.20	0.30	B
Perfume	0.10	0.25	B
CI 42045 (Acid blue 1)	-	0.0001	B
Triethanolamine	-	0.30	C
Dimethicone[6]	0.20		C
Silicone Premix[7]	0.20	1.00	C
Water	qs	qs	

1) Carbopol Ultrez 10 supplied by BF Goodrich
2) Carbopol 934 supplied by BF Goodrich
3) Polymer JR30M supplied by Amerchol
4) Coolact P supplied by Takasago
5) Cremophor RH-60 supplied by BASF
6) DC200 supplied by Dow Corning
7) Any of Silicone Premix Examples I - VI

All of ingredients A are added to water and stirred thoroughly under ambient conditions until a homogenous solution is obtained. All of ingredients B are mixed together and then added to the homogenous solution of ingredients A. All of ingredients C are then added and the resulting solution is thoroughly mixed.

EXAMPLES IX-X

Ingredient (wt. %)	IX (Cream)	X (Balm)	
Carpopol Ultrez 10[1]	-	0.40	A
Acrylates/C10-30 alkyl acrylate cross polymer[2]	0.60	-	A
Cetyl alcohol[3]	1.00	-	B
Stearyl alcohol	1.00	1.50	B

Ammonium lauryl sulphate[4]	-	0.20	B
PEG100 stearate[5]	0.13	-	B
Polyquaternium 10[6]		0.10	C
Phenyl M'Q resin[8]		0.10	C
Silicone Premix[8]	0.50	-	C
Ethanol (denatured)	30.00	15.00	C
l-isopulegol[7]	0.50	0.05	C
lactic acid	0.15	0.10	C
phenoxyethanol	0.20	0.20	C
DMDM hydantoin	-	0.05	C
tetra sodium EDTA	-	0.30	C
Perfume	1.00	0.80	C
Triethanolamine	0.40	0.20	D
Water	qs	qs	

1) Carbopol Ultrez 10 supplied by BF Goodrich
2) Pemulen TR2 supplied by BF Goodrich
3) Crodacol C-95 supplied by Croda Inc.
4) Empicol AL30 supplied by Albright & Wilson
5) Myrj 59 supplied by ICI Surfactants
6) Polymer JR30M supplied by Amerchol
7) Coolact P supplied by Takasago
8) Any of Silicone Premix Examples I - VI

All ingredients of A are solublised in water and then heated to 80°C. All of ingredients B are then added. The solution is then cooled by recirculation to 30°C through a plate heat exchanger with simultaneous high shear mixing. The cooling rate is maintained at between 1.0 and 1.5°C/min. Approximately 50% of ingredient D, triethanolamine, is then added and the solution is mixed until homologous. All of ingredients C are then added and the resulting solution is high shear mixed until homogenous particle size distribution is achieved. Recirculation is then stopped to prevent shear stress damage to the product during completion of neutralisation. The remaining ingredient D is added until the specified pH and viscosity are reached.

All of the exemplified compositions will provide good hair shine, clean hair feel and refreshment, without excessive drying out of the scalp.